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CRADA Final Report
for CRADA Number ORNL95-0359

MICROWAVE PROCESSING OF MATERIALS*

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Lambda Technologies, Inc.

*Research sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Materials Program, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

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MICROWAVE PROCESSING OF MATERIALS
CRADA 95-0359

ABSTRACT

A Cooperative Research and Development Agreement (CRADA) between Lockheed Martin Energy Systems, Inc. (LMES) and Lambda Technologies, Inc. (Lambda) of Raleigh, N.C., was initiated in May 1995. [Lockheed Martin Energy Research, Corp. (LMER) has replaced LMES]. The completion date for the Agreement was December 31, 1996. The purpose of this work is to explore the feasibility of several advanced microwave processing concepts to develop new energy-efficient materials and processes. The project includes two tasks: (1) commercialization of the variable-frequency microwave furnace (VFMF); and (2) microwave curing of polymer composites.

The VFMF, whose initial conception and design was funded by the Advanced Industrial Concepts (AIC) Materials Program, will allow us, for the first time, to conduct microwave processing studies over a wide frequency range. This novel design uses a high-power traveling wave tube (TWT) originally developed for electronic warfare. By using this microwave source, one can not only select individual microwave frequencies for particular experiments, but also achieve uniform power densities over a large area by the superposition of many different frequencies.

OBJECTIVES

The long-term objective of this CRADA is to develop and commercialize versatile, wideband microwave processing facilities using high-power traveling wave tubes originally designed for radar amplifiers. The specific objectives include the further studies on polymeric materials processing via variable-frequency microwaves (VFM) and the development and commercialization of the VFMF.

ATTAINMENT OF OBJECTIVES

Microwave furnace development was achieved in several ways: The benchtop furnace was modified to include an air-actuated press to enable consolidation of prepreg laminates. The press allows us to apply as much as 0.414 MPa (60 psig) over a variety of sample configurations. Additionally, in collaboration with Lambda, we have designed and fabricated a plasma chamber in which we have conducted preliminary hydrogen/methane plasma experiments.

Lambda has developed a computer model using the finite-difference time domain (FDTD) to identify the cause and to predict the location of hot spots. This model demonstrates the advantage of a variable-frequency microwave source when compared with a single-frequency microwave source in that the simulations indicate a "well-stirred" cavity. Experiments confirm the model results.

SPONSOR BENEFITS

The Department of Energy (DOE) supplied funds for the work done by Oak Ridge National Laboratory (ORNL) through the DOE Energy Research Laboratory Technology Transfer Program Office (ER) and the Energy Efficiency and Renewable Energy Division (EE). The benefits to ER with this DOE funding are that ORNL developed engineering designs for high-power systems and worked with Lambda to refine the design concepts for low-power benchtop systems. These designs evolved into Lambda's Vari-Wave product line, which was officially launched in the spring of 1996.

Of interest to EE, ORNL demonstrated microwave curing of advanced resins, polymer matrix composites, and adhesives. Plasma formation and control at various frequencies was also studied. Two U.S. Patents were issued, and five more patents are pending.

The CRADA project yielded several developments that are of substantial benefit for Lambda and ORNL. Lambda's contributions to the project include several major activities: (1) Design and commercialization of a complete line of microwave heating systems. Lambda's customers include universities and private industry. The products are being used for applications in materials, microelectronics, food, and consumer products. (2) Extensive modeling and experimental verification of the relationship of bandwidth to heating uniformity. (3) Experimental work on polymer curing and post curing, complementing ORNL's work and leading to a new theory for microwave heating in composites when conductive phases are present. (4) Closed-loop control and diagnostic routines to better apply VFM technology.

Benefits to ORNL are threefold: (1) the successful commercialization of our VFMF technology; (2) the strengthening of our patent portfolio through the creative contributions of Lambda's engineers; and (3) the improved understanding of the microwave heating process, including novel techniques to model and experimentally map the microwave power distribution in a highly overmoded cavity.

Some benefits to DOE include new industrial uses for microwave technologies that were developed under Fusion Energy and other ER programs. Additionally, we improved techniques for manufacturing lightweight composites of interest to the automobile industry. Economic benefits include regional economic development through the formation and growth (now 17 employees) of a new company in Raleigh, N.C. Through these newly created jobs, export sales are expected to be impacted. Also, new environmentally friendly and cost-effective manufacturing methods for high value-added consumer and electronic products have been demonstrated.

TECHNICAL DISCUSSION

Polymer matrix composites

Polymer matrix composites (PMCs) have several characteristics that make them very appealing as material substitutes in such industries as automotive, aerospace and aircraft, marine, recreation, and defense. PMCs are favored because they are lightweight and exhibit high strength and stiffness. However, their acceptance in high-volume manufacturing, especially autos, has been hindered by the high cost of lay-up, molding, and curing processes; of these, curing makes up approximately 50% of the time involved. If a method could be introduced to reduce the time involved, and therefore, the cost, polymer matrix composites could be used in a much broader range of applications. Microwave processing shows promise for the rapid processing of PMCs. Microwave heating has the advantage over conventional thermal processing of volumetric heating and also the possible enhancement of physical and mechanical properties. Curing of thermosetting laminates via microwaves was studied to examine possible reduction in processing time and to evaluate the resulting mechanical and physical properties. Prior work focused on the use of microwaves to cure PMCs; however, only fixed-frequency systems were employed, primarily because of the ready availability of magnetrons at this frequency. However, it has been shown that sweeping the frequency improves heating uniformity through the superposition of many independent modes within the microwave cavity.

Studies were conducted on glass-fiber polymer matrix composites. Thermal profiles were obtained for PMC plates heated using either fixed-frequency or variable-frequency microwave irradiation. Black-body probes were used to more accurately measure the temperature of the plates. It was found that the variable-frequency heating profile very closely matched the fixed-frequency heating profile; however, by using the variable frequency, the post-curing time was cut from over 8 h to <2 h, while maintaining comparable mechanical properties.

Previously, curing a carbon-fiber crossply lay-up using microwaves was thought to be unattainable. We have been the first to demonstrate that with variable-frequency microwaves, carbon-fiber PMCs can be cured. The temperature of unidirectional carbon-fiber PMCs rises at a rapid rate, but the multidirectional carbon-fiber PMCs heat at a slower rate; however, the multidirectional samples do eventually reach the cure temperature. It was demonstrated that not only did we homogeneously cure the laminates, but our processing actually improved the properties of the material. Differential scanning calorimetry was employed to determine the glass transition temperature of the laminate. Conventional processing gives a glass transition temperature (T_g) of approximately 175°C, whereas VFM processing gives an average T_g of 184°C.

Thermosetting Adhesives Studies

Structural adhesives often require long cure times that translate into elevated per-part costs. In order to make the use of adhesives for primary structures, a reality in high-production-rate consumer goods industries, technologies for reducing the cure time of the adhesive must be developed. Adhesive bonding through the application of VFM radiation has been evaluated as an alternative curing method for joining composite materials or metals, to themselves or each other. The studies showed that the required cure time of a thermosetting epoxy adhesive is substantially reduced by the use of variable-frequency microwaves when compared with conventional (thermal) curing methods. Variable-frequency microwave processing appeared to yield a slight reduction in the required adhesive cure time when compared with processing by the application of single-frequency microwave radiation. In contrast to the single-frequency processing, the variable-frequency methodology does not readily produce localized overheating (burnt or brown spots) in the adhesive or the composite. As a result handling and location of the sample in the microwave oven are less critical for producing high-quality bonds and it allows for a more homogeneous distribution of the cure energy. Variable-frequency microwave processing is a valuable alternative method for rapidly curing thermoset adhesives at low-input power levels.

The first system evaluated comprised glass slides adhesively bonded using VFM processing with a center frequency of 5.03 GHz over a range of input powers and frequency-sweep ranges. In the high-power range, the experimental data indicate that the cure time is roughly equal to input power; for the lower-input power region, the input power is inversely proportional to the exposure or cure time. With the variable frequency, much less input power was required to achieve curing.

Cure times below 15 min, which correspond to input powers in the region of 200 W, produced samples with a significant volume fraction of bubbles in the as-cured adhesive. Note that 200 W is the maximum input power available in this specific microwave system. It is likely that the volumetric energy deposition into these samples occurred too rapidly, causing excessive heating of the adhesive prior to sufficient crosslinking, which would have prevented the outflow of the adhesive or generation of bubbles. As a result, there exists an upper threshold of energy for curing a given adhesive in a given component geometry. As the input power was *decreased*, the time required for complete crosslinking was *increased*. At sufficiently low-power inputs, crosslinking would not be promoted. For this material system and specimen geometry, the lower threshold is below 125 W. Therefore, for this adhesive/substrate material combination, variable frequency microwave system, and processing conditions, the effective curing range of the adhesives is between 125 and 200 W, and the complete cure can be achieved in as little as 15 min. Note that the upper and lower power thresholds for the variable-frequency processing were much lower than for the single-frequency processing. This differential indicates that, from an energy standpoint, variable-frequency processing may be much more efficient for this type of operation.

The second system evaluated was a glass fiber-reinforced isocyanurate composite. The composite was adhesively bonded under the same conditions as the glass slides. The data revealed that the effective curing range of the adhesive is between 150 and 200 W. Additionally, the optimal cure time was 15 min, which is longer than the 12 min required by the single-frequency radiation. However, this may be related to the lower power level available in the variable-frequency furnace used in this work; perhaps the higher-power level is needed to heat the substrate.

Mechanical evaluation revealed that the samples processed in VFMF for 12 to 14 min had strengths and total elongations far below those of conventionally processed samples or the microwave samples cured for longer periods of time at lower energies. Post-failure analysis revealed that these samples contained bubbles characteristic of a material that underwent too high an energy deposition during curing. This same phenomenon has been previously noted where the same adhesive was thermally cured at too high a temperature. The samples processed at lower-input energies for longer times had ultimate strengths almost identical to those of thermally cured samples. The total elongation (i.e., ductility) of the samples microwaved between 22 and 30 min was slightly greater than that of thermally cured samples. Thus equivalent failure strengths and increased ductility were noted at cure times that were between 1/2 and 2/3 those required for conventional curing. The increased ductility for variable-frequency processed samples was not as extensive as that noted for single-frequency processed samples. Further studies are required in this area to find an explanation for this observation.

Some conclusions drawn from this work are that the resultant energy deposition profile is more uniform for variable frequency microwave systems than for VFM systems. As a result, VFM curing is fairly independent of sample placement in the oven, but fixed-frequency curing is highly position sensitive. Contrary to fixed systems, samples cured in VFMFs are processed with less generation of localized hot spots, which gives better quality bonds. Also, the VFM technology represents a valuable alternative method for rapidly curing thermoset adhesives at low-input power levels. For the substrates and adhesive used in this project, surprisingly low levels of input power were required for processing. Additionally, the application of microwave processing for joining substrates using epoxy-based adhesives significantly reduces the curing time to only a third to a quarter of the conventional cure time.

Development of Vari-Wave Instrumentation Products

Lambda provided support at their facility for some of the process trials discussed above. However, Lambda's major effort was in the commercialization and design, followed by market introduction, of a new line of instruments based on VFMF technology, trademarked **Vari-Wave™**. The **Vari-Wave™** product line was officially launched in the spring of 1996.

Vari-Wave™ instrumentation provide the research and quality audit communities with the capability to uniformly control energy distribution (heating) and selectively tune frequency to target materials or molecular structure, while simultaneously monitoring sample characteristics for phase shift, extent of cure and/or dielectric properties. **Vari-Wave™** combines a software-driven, microprocessor control package with a sweep oscillator, broadband amplifier, and precision microwave cavity that provides the following features:

- Automatic diagnostic routines (cavity characterization) that enable optimum process conditions to be set for various sample materials and determine sample signature analysis for quality audit capability.
- Automatic cycle control that permits electrical tuning for material property changes during the process cycle.
- Controlled and uniform distribution of 150 to 200 W of microwave energy that produces uniform heating properties.
- Selectively tuned microwave frequency from 2.4 to 7.5 GHz or 6.5 to 18 GHz that permits capability tc selectively heat targeted molecular structure.
- Accurately measured and controlled temperature profile throughout a cycle.
- Measured dielectric loss properties of sample materials with single mode option.
- Complete instrumentation capability in a cost-effective, tabletop unit.

The **Vari-Wave™** instrument incorporates the fundamental and patented theory of applying a frequency agile power source into a precision-designed cavity to ensure uniform energy distribution (VFMF). Inherent to that capability, the instrument must contain a sweep oscillator, a power amplifier, temperature measurement and control, and a closed-loop control circuit with analytical data acquisition features. On an individual basis and for basic instrumentation alone, this type capability could cost in excess of $150,000. **Vari-Wave™** provides all that capability plus a precision cavity and temperature control for one-third of the cost.

Prior to **Vari-Wave™** product packaging, VFM technology was thought to be *expensive and complicated* due to the equipment and controls required to produce frequency agile systems. The **Vari-Wave™** product provided VFM capability plus a broad range of diagnostic and analytical features at *a competitive price range, and it is packaged in a table top, easy-to-use instrument.*

Vari-Wave™ products are currently being used for research in the following application areas:

- Curing of advanced polymer materials and polymeric composites (large areas and at rates 10 to 15 times faster than conventional thermal cure);
- Chemical synthesis and reaction enhancement (8 to 10 times conventional heat);
- Curing of adhesives for bonding dissimilar materials, such as silicon or metal to composite and/or glass (automotive panels, electronic assemblies and consumer products - at rates 10 times faster and without overheating adjacent components that are sensitive at the adhesive cure temperature);
- Selective heating required for cofiring ceramic/composite samples;
- Measurement of material properties, such as dielectric loss tangent;
- Curing of encapsulant materials on electronic circuits, for chip-on-board and flip-chip assemblies (20 to 30 times faster without damage to circuits);
- Biomedical research of frequency effects on targeted molecular structures;
- Waste remediation studies for irradiating target contaminants; and
- Quality control of moisture level and deformation of standard product profile.

INVENTIONS

Several invention disclosures and patents arose as a result of the CRADA. The background patent (U.S. Patent No. 5,321,222), "Variable Frequency Microwave Furnace System," was issued June 1994. Also issued was "Apparatus and Method for Microwave Processing of Materials," U.S. Patent No. 5,521,360. Several patent applications were filed: "Process for Curing Polymers," ESID 1378-X; "Improved Microwave Tube," ESID 1581-X; "Improved Microwave and Radio Frequency (RF) Load," ESID 1582-X; "Method for Joining Carbon-Carbon Composites to Metals," ESID 1592-X; and "Adhesive Bonding Using Variable Frequency Microwave Energy," ESID 1812-XC.

COMMERCIALIZATION

Lambda is actively commercializing the VFMF. The new product line (trademark Vari-Wave) with the new VFM control algorithm was officially launched at the Materials Research Society Spring Meeting, April 1996. Several units have been delivered to large U.S. institutions and one in Europe. These sales include major electronics manufacturers, a large biomedical company, and major materials research universities. The company has grown to approximately 17 people and is expanding into larger facilities in the spring of 1997.

PLANS FOR FUTURE COLLABORATION

At this time, Lambda is interested in pursuing a small CRADA to further investigate microwave adhesive bonding of metal-to-metal and metal-to-composite assemblies, primarily aimed at the automobile industry. Lambda is also interested in uses of the VFMF in the biotechnology area. Funding is now being sought to pursue these opportunities.

CONCLUSIONS

The CRADA between LMER and Lambda has been successfully completed. Several materials of industrial interest were examined. It was found that processing with variable-frequency microwaves significantly decreased processing time, frequently decreased the power required for processing, and often enhanced physical and mechanical properties. Some materials previously believed impossible to process using microwaves were shown to be amenable to variable-frequency processing, including multidirectional carbon fiber prepreg laminates and metal samples. A large body of intellectual property was created, and a licensing agreement was executed. Furthermore, a new instrument that economically incorporates the VFMF technology is available to the research community, which will further advance new applications using this technology.

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